PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C03B 19/14, C03C 3/06, C03B 32/00

A1

(11) International Publication Number: WO 00/39038

(43) International Publication Date: 6 July 2000 (06.07.00)

(21) International Application Number: PCT/EP99/10282

(22) International Filing Date: 22 December 1999 (22.12.99)

(30) Priority Data:
10/371084 25 December 1998 (25.12.98) JP

(71) Applicants (*for all designated States except US*): HERAEUS QUARZGLAS GMBH & CO. KG [DE/DE]; Quarzstrasse, D-63450 Hanau (DE). SHIN-ETSU QUARTZ PRODUCTS CO., LTD. [JP/JP]; 22-2, Nishi-Shinjuku 1-chome, Shinjuku-ku, Tokyo 160-0023 (JP).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): FUJINOKI, Akira [JP/JP]; 1-6-12, Midorigaoka-nishi, Koriyama-shi, Fukushima 963-0701 (JP). OSHIMA, Takayuki [JP/JP]; Asaka Dormitory #206, 2-46, Hideno-yama, Asaka-machi, Koriyama-shi, Fukushima 963-0101 (JP). NISHIMURA, Hiroyuki [JP/JP]; Asaka Dormitory #102, 2-46, Hideno-yama, Asaka-machi, Koriyama-shi, Fukushima 963-0101 (JP).

(74) Agent: KÜHN, Hans-Christian; Heraeus Holding GmbH, Schutzrechte, Heraeusstrasse 12-14, D-63450 Hanau (DE).

(81) Designated States: US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHOD FOR PRODUCING OPTICAL QUARTZ GLASS FOR EXCIMER LASERS

(57) Abstract

An object of the present invention is to provide a method for producing a large optical quartz glass for use in excimer lasers, which exhibits high transmittance to excimer laser radiations and which is yet resistant to lasers. This problem can be solved by a method for producing an optical quartz glass for use in excimer lasers, comprising a step of forming a porous silica preform by depositing soot-like silica formed by flame hydrolysis of a high-purity volatile silicon compound, a step of obtaining a quartz glass body by heating the porous silica preform in an oxidizing atmosphere and vitrifying the resulting body into a transparent body, and a step of performing a heat treatment in a reducing atmosphere comprising hydrogen. The oxidizing heat treatment generates oxygen defects, the hydrogen treatment results in a silica body doped with hydrogen molecules and free of said defects.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Patent Application

Heraeus Quarzglas GmbH & Co. KG
Shin Etsu Quartz Products Co., Ltd.

Method for Producing Optical Quartz Glass for Excimer Lasers

Detailed Description of the Invention

[0001]

Industrial Field of Application

The present invention relates to a method for producing an optical quartz glass for use in excimer lasers, and in further detail, it relates to a method for producing an optical quartz glass for use in the optical system of a lithographic system using an excimer laser radiation as the light source; in a still further detail, it relates to a method for producing a synthetic quartz glass for use in the optical system of an ArF excimer laser lithographic system, such as a lens, a prism, or a beam splitter.

[0002]

Prior Art

With the recent increase in the degree of integration in LSIs (large scale integrated circuits), the integrated circuit patterned on wafers are becoming finer, and mass production of Ultra LSIs provided with ultrafine patterns in the order as fine as quarter micron (0.25μm) or even more is now under way. To obtain such ultrafine patterns, it is necessary to use aligner

light sources having still shorter wavelength, and, steppers using excimer laser radiation as the light source had been developed. Steppers equipped with KrF excimer laser radiation (248 nm in wavelength) is already put into practical use, and steppers using ArF excimer laser radiation (193 nm in wavelength) as the light source is attracting much attention as a promising stepper of the next generation. As a glass material which exhibits sufficiently high transmittance in the short wavelength region of the KrF excimer laser and ArF excimer laser radiations, there can be mentioned a quartz glass, fluorite, etc. Particularly among them, a synthetic quartz glass prepared by fusion and vitrification of a product obtained by flame hydrolysis of a high purity silicon compound and the like is preferred as an optical material for lithography using excimer laser radiation as the light source, because it exhibits high transmittance in the short wavelength region of 260 nm or less.

[0003]

Problems the Invention is to Solve

However, if excimer laser radiations such as those of the KrF excimer lasers and ArF excimer lasers are irradiated for a long duration of time to the synthetic quartz glass above, paramagnetic defects known as E' centers or NBOHC (non-bridging oxygen hole centers) generate inside the synthetic quartz glass as to impair long time stability, because the excimer lasers yield high energy pulse radiations with a life of about 20 nanoseconds. As a means to solve such problems, in JP-A-Hei3-88742 (the term „JP-A-„ as referred herein signifies „an unexamined published Japanese patent application") is proposed a method of doping the synthetic quartz glass body with hydrogen. However, this method may lead to a generation of reducing defects in the synthetic quartz glass during its production process, and these defects easily undergo decomposition upon irradaition of the excimer laser radiation and yield paramagnetic defects. The resulting defects then generate an undesirable absorption band at a wavelength of 215 nm, thereby considerably deteriorating the transmittance of excimer laser radiations, particularly, that of the ArF excimer laser radiations. The paramagnetic defects above are the oxygen deficient type defects which generate as a result of the combination of Si in the quartz glass structure (SiO_2) with less than stoichiometric quantity of oxygen. In JP-A-Hei6-166528 is proposed a method of preventing the generation of these parametric defects from occurring, which comprises subjecting the quartz glass to an oxidation treatment in the temperature range of from 600 to 1500 °C under an atmosphere containing oxygen, followed by a treatment in the temperature range of from 300 to 600 °C under an atmosphere containing hydrogen. This method certainly is a remedy for preventing paramagnetic defects from occurring; however, since it incorporates a thermal treatment performed in a plurality of steps, impurities which diffuse from

the outside lower the transmittance of the synthetic quartz glass due to contamination. It is a still other disadvantage that the process requires a long duration of time in producing a large scale quartz glass member, because the diffusion rate of hydrogen in the synthetic quartz glass body remains too low in a heat treatment that is performed in such a low temperature range of from 300 to 600 °C. In particular, with the recent trend in the increase of exposure area, thick and large aperture optical systems are required; in such cases, hydrogen treatment in the above temperature range requires several months or longer, and this makes the process industrially unfeasible. Further, in Japanese Patent No. 2566151 (JP-A-Hei1-197335) is proposed a method similar to above, which comprises producing quartz glass by subjecting a bulk of synthetic quartz glass to an oxidation treatment that is followed by hydrogen treatment. However, this production method also suffers a disadvantage such that the oxygen deficient defects cannot be sufficiently removed from the thick and large aperture optical members which meet to the recent requirements, because the method requires an oxidation treatment of a bulk quartz glass. In the light of such circumstances, there is a keen demand for a proposal of an optical member suitable for thick and large aperture optical systems having excellent transmittance of excimer laser radiations, particularly, ArF excimer laser radiations, and yet, having superior resistance against laser radiations.

Accordingly, the present inventors intensively continued studies, and, as a result, they have found that, to efficiently recover the reducing defects which generate in a synthetic quartz glass during hydrogen treatment, it is effective to first form oxygen excessive defects inside the quartz glass, and to then treat the resulting product in hydrogen. Further, in the treatment above, the soot-like silica generated by flame hydrolysis of a high purity volatile silicon compound is deposited to obtain a porous silica preform (referred to hereinafter as „a soot preform"), and the soot preform is subjected to an oxidation treatment while elevating the treatment temperature to 800 °C or higher. In this manner, oxygen sufficiently diffuses into the inner side of a large glass body as to generate oxygen excessive defects, and by subjecting the resulting product to a hydrogen treatment at a temperature higher than 600 °C, it was found that an optical quartz glass free from generation of reducing defects and doped with hydrogen molecules at a high concentration can be obtained with high transmittance for excimer laser radiations, particularly, ArF excimer laser radiations, still having excellent resistance against laser radiations. The present invention has been accomplished based on these findings. That is:

[0005]

An object of the present invention is to provide a method for producing an optical quartz glass for excimer lasers having high transmittance and yet having excellent resistance against laser radiations.

[0006]

Another object of the present invention is to provide a method for producing a thick and large aperture optical quartz glass for ArF excimer lasers having high transmittance for ArF excimer laser radiations, and yet having excellent resistance against laser radiations.

[0007]

Means for Solving the Problems

The object above is accomplished by a method for producing an optical quartz glass for use in excimer lasers, comprising a step of forming a porous silica preform by depositing soot-like silica formed by flame hydrolysis of a high-purity volatile silicon compound, a step of obtaining a quartz glass body by heating the porous silica preform in an oxidizing atmosphere and vitrifying it into a transparent body, and a step of performing a heat treatment in a reducing atmosphere.

[0008]

As high purity volatile silicon compounds, there can be mentioned silicon tetrachloride, methyl trimethoxysilane, tetramethoxysilane, etc., and the soot-like silica produced by subjecting them to flame hydrolysis is deposited on a rotating heat-resistant base body to form a porous silica preform. The porous silica preform is then heated in an oxidizing atmosphere for vitrification to obtain a transparent body. The heating is preferably performed in a temperature range not lower than 1400 °C, but not higher than 1600 °C. Preferably, the porous silica preform is pre-sintered in a temperature range of from 1000 to 1400°C in an oxidizing atmosphere for densification, and then heated in a temperature range of from 1400 to 1600°C in an inert gas atmosphere. By thus treating in an oxidizing atmosphere, a quartz glass body having oxygen excessive defects is produced. The oxygen excessive defects are the defects that are formed by the combination of Si in the quartz glass structure (SiO_2) with oxygen at an amount not less than the stoichiometric quantity. As the gas for use in the oxidizing atmosphere, there can be used a mixed gas comprising oxygen with an inert gas, such as gaseous He or N_2, but particularly preferred is gaseous He. In the mixed gas above, gaseous oxygen preferably accounts for 30 % by volume or more but less than 100 %. If the oxygen content is less than 30 % by volume, the oxygen deficient defects account too low as result in an insufficient recovery of the

reducing defects. It is not preferred to use 100 % gaseous oxygen because bubbles may remain in the quartz glass. Subsequent to this treatment in an oxidizing atmosphere, a homogenization treatment, or a homogenization treatment and molding (referred to hereinafter as „a homogenization treatment and the like") is performed in order to highly homogenize the optical member. The layered structure, as well as the striae as the like in the three directions, which generates during the deposition of the soot-like silica is removed by the homogenization treatment and the like, thereby resulting in a highly homogeneous quartz glass having a refractive index distribution (Δn) of 2×10^{-6} or lower, or a birefringence of 2 nm/cm or lower. However, since the homogenization treatment is performed by maintaining the product at a high temperature of 1600 °C or higher for a long duration of time in a refractory furnace, contamination of the quartz glass occurs because impurities diffuse into the quartz glass from the furnace material, jigs, and the atmosphere. In particular, the contamination attributed to Na is serious, because the incorporation of Na greatly impairs the transmittance for ArF excimer laser radiations. In this context, in JP-A-Hei7-267662 is proposed a homogenization treatment which is performed free of furnace materials. Molding of the quartz glass is performed after the homogenization treatment, in which the quartz glass body is shaped into an optical material having the desired shape of, for example, a column, a disk, or a tetrahedron. The molding is performed, in general, by heating the quartz glass body in a crucible at a temperature not lower than 1600°C or higher to allow the body to deform in accordance with its own weight or forcibly. Thus, the quartz glass molding undergoes contamination again due to the thermal diffusion of Na during the molding process.

[0009]

In the process according to the present invention, a heat treatment under a reducing atmosphere is performed subsequent to the heat treatment in an oxidizing atmosphere and the homogenization treatment and the like described above. As the reducing atmosphere usable for the treatment, mentioned is a gaseous hydrogen atmosphere, or an atmosphere of mixed gas containing hydrogen and an inert gas. The heating temperature is in a range of 600 to 1500 °C, and preferably, the range is from 800 to 1000 °C. If the temperature should be lower than 600 °C, the effect of the treatment is low; if the treatment should be performed at a temperature higher than 1500 °C, an increase in the effect cannot be expected. Even if such a high temperature heat treatment is performed under a reducing atmosphere, the quartz glass not only remains free from reducing defects, but also is doped with hydrogen molecules at a high concentration, thereby resulting in a product having stability against the irradiation of excimer

laser radiations. Since the stability against the irradiation of excimer laser radiations increases in proportion to the content of hydrogen, it is preferred to apply pressure during the heat treatment under the reducing atmosphere. The pressure is preferably applied at 1 atm or higher but not higher than 10 atm. If the applied pressure should exceed 10 atm, the treatment is categorized as a hydrogen treatment under a high temperature and high pressure; hence, it happens that such a treatment should follow some regulations under a law. The oxygen excessive defects that are contained in the quartz glass molding undergo reduction during the treatment under the reducing atmosphere to newly generate OH groups and produce hydrogen molecules that are doped in the quartz glass. The concentration of the hydrogen molecules is preferably 2×10^{17} molecules/cm^3 or higher. An annealing treatment follows the heat treatment under the reducing atmosphere, and this annealing treatment is performed by maintaining in the temperature range of from 1100 to 1200 °C in air for a long duration of 10 hours or longer. After the annealing treatment, the temperature is gradually lowered to 600°C at a cooling rate of 50 °C/hour, and then left to natural cooling. A cooling rate higher than the range above is not preferred because cracks may generate during the cooling. Although the annealing treatment is performed at a low temperature in the vicinity of the cooling point (1120°C) of the quartz glass, impurities which diffuse out from the furnace material and the atmosphere and the like contaminates the quartz glass in a manner similar to the case of homogenization treatment and molding. If the content of Na in the quartz glass molding falls in a range of from 24 to 60 ppb due to the contamination during the homogenization treatment, molding, or annealing treatment, the transmittance can be recovered by irradiating a continuous ultraviolet radiation of 260 nm or shorter for a long duration of time; particularly, in case of an ArF excimer laser radiation, the internal absorption can be recovered to within 0.2 %. As the lamp for use irradiating the continuous ultraviolet radiation above, there can be employed a low vapor pressure mercury lamp radiating a radiation having a principal wavelength of 253.7 nm and 184.9 nm, a Xe excimer lamp which radiates a light having a wavelength of 172 nm, or a KrCl excimer lamp which radiates a light having a wavelength of 222 nm. The luminance of the ultraviolet radiation is preferably 1 mW/cm^3 or higher, and the duration of irradiation is preferably 50 hours or longer.

[0010]

Embodiment of the Invention

Preferred embodiments according to the present invention are decribed below by way of examples, but it should be understood that the present invention is by no means limited thereto.

[0011]

Examples

The physical properties described below in Examples and Comparative Examples are values obtained by the measuring methods as follows.

i) Distribution of refractive indices: Measurements were made using a Fizeau's interferometer.

ii) Birefringence: Measurements were made in accordance with crossed nicol method.

iii) Striae: Visual observation.

iv) Internal transmittance of light 193 nm in wavelength: Apparent transmittance T % was obtained at a thickness of 10 mm, and a reduced value was calculated in accordance with the equation (T/90.68) × 100, where 90.68 % is a value obtained by subtracting the loss, i.e., 0.18 %, known to be attributed to Rayleigh scattering, from the theoretical transmittance 90.86 % of the quartz glass for a light 193 nm in wavelength.

v) Na concentration: The value was obtained by a measurement using flameless atomic absorption spectroscopy.

[0012]

Example 1

Soot-like silica was prepared by means of flame hydrolysis comprising introducing silicon tetrachloride accompanied by gaseous oxygen into an oxyhydrogen flame, and was deposited on a rotating heat-resistant base body to obtain a soot body. The soot body thus obtained yielded a low density on the outer side thereof, whereas the inner side exhibited a relatively high density. The average bulk density of the soot body was found to be 1.2 g/cm^3. The resulting soot body was subjected to pre-sintering so that it may yield a homogeneous density by perfor-

ming heating at 1000 °C for a duration of 8 hours in an oxidizing atmosphere consisting of 80 % by volume of oxygen and 20 % by volume of He. The bulk density of the soot body was increased to 1.5 g/cm^3 by the pre-sintering, and the refractive index distribution was decreased. Then, the temperature inside the furnace was elevated to 1450 °C in an oxidizing atmosphere consisting of 50 % by volume of oxygen and 50 % by volume of He, and by pulling up, the soot body was vitrified to obtain a transparent body . The OH concentration of the thus obtained quartz glass body was found to be 20 ppm, but no hydrogen was detected. The resulting quartz glass body was mounted on a graphite crucible, and was heated to 1800 °C under a nitrogen-purged atmosphere so as to obtain a molding by its own weight into a disk having an outer diameter of 250 mm and a height of 100 mm.

[0013]

Of the thus obtained molding, the portion that was brought into contact with the peripheral graphite was sufficiently removed by HF etching treatment, and the resulting molding was subjected to hydrogen loading in a high pressure hydrogen treatment furnace by heating it at 1100 °C for a duration of 24 hours under a hydrogen pressure of 10 atm. Subsequent to the treatment, annealing treatment of the molding was performed. The annealing treatment was performed by maintaining it at 1150 °C for a duration of 20 hours under a hydrogen pressure of 1 atm, followed by cooling to 600 °C at a cooling rate of 5 °C/hour, and, from that temperature, the molding was allowed to cool naturally to carry out the strain removal operation. The refractive index distribution (Δn) was found to be 1×10^{-6}, and the birefringence was 1 nm/cm or lower. No striae in three directions nor layer structure was observed. The concentration of OH groups was 65 ppm, and that of the hydrogen molecules was 2.5×10^{18} molecules/cm^3. A specimen 60 mm in diameter and 10 mm in height was cut out of the molding to measure the transmittance thereof. Then, ArF excimer laser radiation was irradiated to the same specimen at an energy density per pulse of 20mJ/cm^2 and a frequency of 200 Hz to observe the change in transmittance and in refractive index. The results are given in Table 1.

[0014]

Example 2

Soot-like silica was prepared by means of flame hydrolysis comprising introducing high purity methyltrimethoxysilane accompanied by gaseous argon into an oxyhydrogen flame, and

was deposited on a rotating heat-resistant base body to obtain a soot body. The average bulk density of the soot body was found to be 1.3 g/cm^3. The resulting soot body was subjected to pre-sintering by performing heating at 900 °C for a duration of 10 hours in an oxidizing atmosphere consisting of 80 % by volume of oxygen and 20 % by volume of He. The bulk density of the soot body was increased to 1.5 g/cm^3 by the pre-sintering, and the refractive index distribution of the entire body was decreased. Then, the temperature inside the furnace was elevated to 1450 °C in an oxidizing atmosphere consisting of 50 % by volume of oxygen and 50 % by volume of He, and by pulling up, the soot body was vitrified to obtain a transparent body. The OH concentration of the thus obtained quartz glass body was found to be 30 ppm, but no hydrogen was detected. Similar to the case described in Example 1, the resulting quartz glass body was shaped to the same size as in Example 1, where the portion that was brought into contact with the peripheral graphite was sufficiently removed by HF etching treatment. Subsequent to the treatment, the resulting molding was subjected to hydrogen loading in a high pressure hydrogen treatment furnace by heating it at 1000°C for a duration of 32 hours under a hydrogen pressure of 5 atm. After the treatment, annealing treatment was performed on the molding. The annealing treatment was performed by maintaining it at 1150°C for a duration of 20 hours under a hydrogen pressure of 1 atm. This was followed by cooling to 600°C at a cooling rate of 5 °C/hour, and, strain removal operation was carried out from that temperature by allowing the molding to be cooled naturally. The refractive index distribution (Δn) was found to be 1×10^{-6}, and the birefringence was 1 nm/cm or lower. No striae in three directions nor layer structure was observed. The concentration of OH groups was 80 ppm, and that of the hydrogen molecules was 1.0×10^{18} molecules/cm^3. A specimen 60 mm in diameter and 10 mm in height was cut out of the molding to measure the transmittance thereof. Then, ArF excimer laser radiation was irradiated to the same specimen to observe the change in transmittance and in refractive index. The results are given in Table 1.

[0015]

Example 3

Soot-like silica was prepared by means of flame hydrolysis comprising introducing high purity tetramethoxysilane accompanied by gaseous argon into an oxyhydrogen flame, and was deposited on a rotating heat-resistant base body to obtain a soot body. The average bulk density of the soot body was found to be 1.3 g/cm^3. The resulting soot body was subjected to pre-

sintering by performing heating at 900 °C for a duration of 10 hours in an oxidizing atmosphere consisting of 80 % by volume of oxygen and 20 % by volume of He. The bulk density of the soot body was increased to 1.5 g/cm³ by the pre-sintering, and the refractive index distribution of the entire body was decreased. Then, the temperature inside the furnace was elevated to 1450 °C in an atmosphere consisting of 100 % by volume of He, and by pulling up, the soot body was vitrified to obtain a transparent body. The OH concentration of the thus obtained quartz glass body was found to be 25 ppm, but no hydrogen was detected. Similar to the case described in Example 1, the resulting quartz glass body was shaped to the same size as in Example 1, where the portion that was brought into contact with the peripheral graphite was sufficiently removed by HF etching treatment. Subsequent to the treatment, the resulting molding was subjected to hydrogen loading in a high pressure hydrogen treatment furnace by heating it at 1000 °C for a duration of 32 hours under a hydrogen pressure of 5 atm. After the treatment, annealing treatment was performed on the molding. The annealing treatment was performed by maintaining it at 1150 °C for a duration of 20 hours under atmosphere. This was followed by cooling to 600 °C at a cooling rate of 5 °C/hour, and, strain removal operation was carried out from that temperature by allowing the molding to be cooled naturally. The refractive index distribution (Δn) was found to be 1×10^{-6}, and the birefringence was 1 nm/cm or lower. No striae in three directions nor layer structure was observed. The concentration of OH groups was 80 ppm, and that of the hydrogen molecules was 1.0×10^{18} molecules/cm³. A specimen 60 mm in diameter and 10 mm in height was cut out of the molding to measure the transmittance thereof. Then, ArF excimer laser radiation was irradiated to the same specimen to observe the change in transmittance and in refractive index. The results are given in Table 1.

[0016]

Table 1

Example	Transmittance at 193 nm	Transmittance after irradiating 1×10^3 pulses	Transmittance after irradiating 2×10^7 pulses	Compaction
1	99.8	99.8	99.7	None
2	99.8	99.8	99.6	None
3	99.8	99.7	99.6	None

[0017]

From Table 1 above, it can be seen that the quartz glass obtained by the production method according to the present invention remains without significant decrease in transmittance and no compaction is observed thereon even after an ArF excimer laser radiation is irradiated for a long duration of time. The compaction herein refers to the shrinking of the quartz glass on irradiating a laser radiation. If the compaction takes place, the refractive index increases and leads to the deterioration of image forming characteristics of the optical system such as the lenses of an aligner.

[0018]

The production method according to the present invention enables a highly laser-resistant optical quartz glass which also has a high transmittance for excimer laser radiations. In particular, the present invention is effective in the production of thick optical quartz glass having large diameter for use in ArF excimer lasers, which is stable and has no drop in transmittance even when it is irradiated by an ArF excimer laser radiation for a long duration of time.

Claims

1. A method for producing an optical quartz glass for use in excimer lasers, comprising a step of forming a porous silica preform by depositing soot-like silica formed by flame hydrolysis of a high purity volatile silicon compound, a step of obtaining a quartz glass body by heating the porous silica preform in an oxidizing atmosphere and vitrifying it into a transparent body, and a step of performing a heat treatment in a reducing atmosphere.

2. A method for producing an optical quartz glass for use in excimer lasers as claimed in Claim 1, wherein the heating temperature in the oxidizing atmosphere is in a range of from 800 °C to 1600 °C.

3. A method for producing an optical quartz glass for use in excimer lasers as claimed in Claim 1, wherein the step of obtaining a quartz glass body comprises densifying the porous silica preform by heating it in an oxidizing atmosphere in a temperature range of from 800 to 1400 °C, and then heating it in an inert gas atmosphere in a temperature range of from 1400 °C to 1600 °C.

4. A method for producing an optical quartz glass for use in excimer lasers as claimed in any of Claims 1 to 3, wherein the oxygen concentration of the oxidizing atmosphere is set in the range of 30 % by volume or higher but less than 100 % by volume.

5. A method for producing an optical quartz glass for use in excimer lasers as claimed in any of Claims 1 to 4, wherein the quartz glass body vitrified into a transparent body is molded and then heat treated in a reducing atmosphere.

6. A method for producing an optical quartz glass for use in excimer lasers as claimed in any of Claims 1 to 5, wherein the heat treatment in the reducing atmosphere is performed in the temperature range of from 600 to 1200°C under a pressure of 1 atm or higher.

7. A method for producing an optical quartz glass for use in excimer lasers as claimed in any of Claims 1 to 6, wherein hydrogen molecules are doped at a density of 1×10^{17} molecules/cm^3 or more in the heat treatment performed under the reducing atmosphere.

8. A method for producing an optical quartz glass for use in excimer lasers as claimed in any of Claims 1 to 7, wherein, after the heat treatment in the reducing atmosphere, annealing treatment is performed by maintaining the temperature in the range of from 1100 to 1200 °C in air, and then gradual cooling is performed at a gradually cooling rate of 50 °C/hour or less.

INTERNATIONAL SEARCH REPORT

Inter ›nal Application No
PCT/EP 99/10282

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03B19/14 C03C3/06 C03B32/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 97, no. 7, 31 July 1997 (1997-07-31) -& JP 09 059034 A (SUMITOMO METAL IND. LTD.), 4 March 1997 (1997-03-04)	1,5-7
Y	abstract page 9, paragraph 86 -page 10, paragraph 87 ---	8
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 3, 31 March 1999 (1999-03-31) & JP 10 330120 A (NIKON CORP.), 15 December 1998 (1998-12-15) abstract	8
P,Y	-& EP 0 921 104 A (NIKON CORP.) 9 June 1999 (1999-06-09) claims 7-17 ---	8
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 March 2000	10.04.00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stroud, J

1

INTERNATIONAL SEARCH REPORT

Inte   onal Application No
PCT/EP 99/10282

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 96, no. 7, 31 July 1996 (1996-07-31) -& JP 08 081225 A (SUMITOMO METAL IND. LTD.), 26 March 1996 (1996-03-26) abstract page 6, column 9, paragraph 51 ---	1-3,5,6
X	PATENT ABSTRACTS OF JAPAN vol. 18, no. 495, 16 September 1994 (1994-09-16) & JP 06 166528 A (SHIN-ETSU QUARTZ PROD. CO. LTD.), 14 June 1994 (1994-06-14) cited in the application abstract ---	1,2,6,7
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 494, 8 November 1989 (1989-11-08) & JP 01 197335 A (SHIN-ETSU QUARTZ PROD. CO. LTD.), 9 August 1989 (1989-08-09) cited in the application abstract ---	1,2
A	EP 0 401 845 A (SHIN-ETSU QUARTZ PROD. CO. LTD.) 12 December 1990 (1990-12-12) cited in the application claims 26-29 -----	1,6,7

1

INTERNATIONAL SEARCH REPORT

Int ıtional application No.
PCT/EP 99/10282

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 99/10282

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-8 relate to a large number of possible methods in respect of the step of heat treatment in a reducing atmosphere. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the methods claimed, namely a method whereby the reducing atmosphere comprises hydrogen to result in a product doped with hydrogen molecules. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is not possible. Consequently, the search has been carried out for those parts of the claims which are clearly supported and disclosed, namely those parts relating to the methods of producing a deposit of silica soot by flame-hydrolysis comprising the step of heat treatment in a hydrogen atmosphere subsequent to the steps of heat treatment in an oxidizing atmosphere and of vitrification, and wherein the silica product produced is doped with hydrogen molecules.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/10282

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
JP 09059034	A	04-03-1997	NONE			
JP 10330120	A	15-12-1998	CN	1219515	A	16-06-1999
			EP	0921104	A	09-06-1999
JP 08081225	A	26-03-1996	NONE			
JP 06166528	A	14-06-1994	JP	2821074	B	05-11-1998
JP 01197335	A	09-08-1989	JP	2566151	B	25-12-1996
EP 0401845	A	12-12-1990	AT	116448	T	15-01-1995
			DE	69015453	D	09-02-1995
			DE	69015453	T	01-06-1995
			JP	3088742	A	15-04-1991
			JP	6053593	B	20-07-1994
			US	5086352	A	04-02-1992
			US	5325230	A	28-06-1994
			JP	3109233	A	09-05-1991
			JP	6027013	B	13-04-1994
			JP	3101282	A	26-04-1991
			JP	6048734	B	22-06-1994
			JP	1898031	C	23-01-1995
			JP	3088743	A	15-04-1991
			JP	6027014	B	13-04-1994